## Nucleophilic substitution with cyanide ions

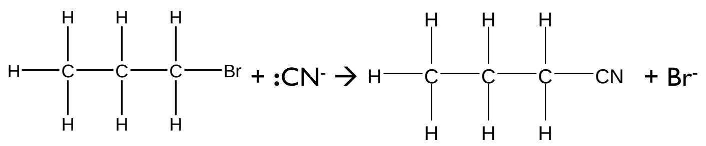
**Change in functional group: halogenoalkane → nitrile**

**Reagent: KCN** dissolved in **ethanol/water mixture**

**Conditions**: Heating under reflux

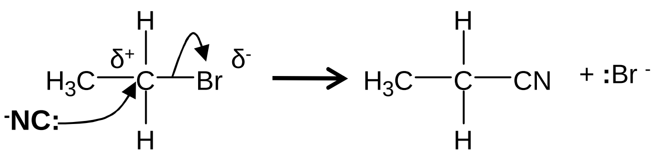
**Mechanism**: Nucleophilic Substitution

**Type of reagent**: Nucleophile, $:CN^-$



1-bromopropane butanenitrile

Note: the mechanism is identical to the above one

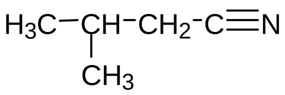


This reaction increases the length of the carbon chain (which is reflected in the name) In the above example butanenitrile includes the C in the nitrile group

**Naming Nitriles**

Nitrile groups have to be at the end of a chain. Start numbering the chain from the C in the CN

$CH_3CH_2CN$ : propanenitrile



3-methylbutanenitrile

Note the naming: but**ane**nitrile and not butannitrile.

## Nucleophilic substitution with ammonia

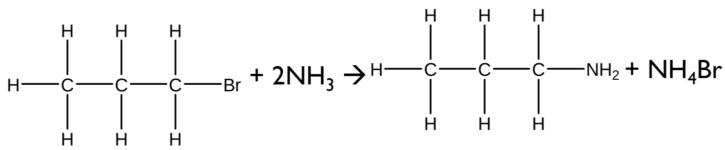
***Change in functional group:*** **halogenoalkane → amine**

**Reagent**: $NH_3$ dissolved in ethanol

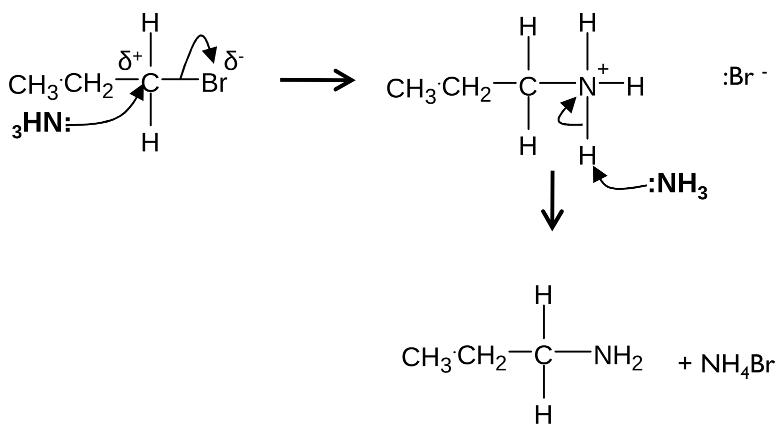
**Conditions**: Heating under pressure (in a sealed tube)

**Mechanism**: Nucleophilic substitution

**Type of reagent**: Nucleophile, $:NH_3$



propylamine



Naming amines:

In the above example prop**yl**amine, the propyl shows the 3 C's of the carbon chain.

Sometimes it is easier to use the IUPAC naming for amines e.g. Prop**an-1-amine**

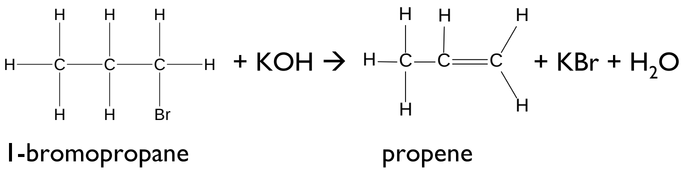
Further substitution reactions can occur between the halogenoalkane and the amines formed leading to a lower yield of the amine. Using excess ammonia helps minimise this.

## 2. Elimination reaction of halogenoalkanes

Elimination: removal of small molecule (often water) from the organic molecule

### Elimination with alcoholic hydroxide ions

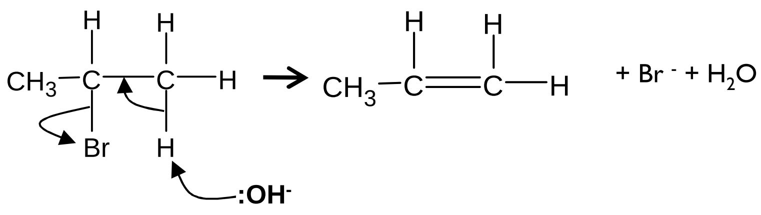
**Change in functional group: halogenoalkane → alkene**
**Reagents**: Potassium (or sodium) hydroxide
**Conditions**: In **ethanol** ; Heat
**Mechanism**: Elimination
**Type of reagent**: Base, $OH^-$




Note the importance of the solvent to the type of reaction here.

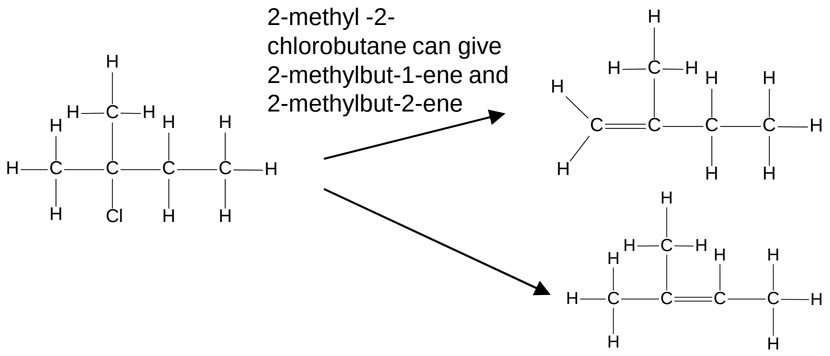
**Aqueous: substitution**

**Alcoholic: elimination**




Often a mixture of products from both elimination and substitution occurs

With unsymmetrical secondary and tertiary halogenoalkanes two (or sometimes three) different structural isomers can be formed




The structure of the halogenoalkane also has an effect on the degree to which substitution or elimination occurs in this reaction.

Primary tends towards substitution

Tertiary tends towards elimination

### Uses of Halogenoalkanes

Chloroalkanes and chlorofluoroalkanes can be used as solvents

$CH_3CCl_3$ was used as the solvent in dry cleaning

Halogenoalkanes have also been used as refrigerants, pesticides and aerosol propellants

Many of these uses have now been stopped due to the toxicity of halogenoalkanes and also their detrimental effect on the atmosphere

### Ozone Chemistry

The naturally occurring ozone ($O_3$) layer in the upper atmosphere is beneficial as it filters out much of the sun's harmful UV radiation.

Ozone in the lower atmosphere is a pollutant and contributes towards the formation of smog.

Man-made chlorofluorocarbons (CFC's) caused a hole to form in the ozone layer.

Chlorine radicals are formed in the upper atmosphere when energy from ultra-violet radiation causes C–Cl bonds in chlorofluorocarbons (CFCs) to break.

$$CF_2Cl_2 \rightarrow CF_2Cl^{\bullet} + Cl^{\bullet}$$

The chlorine free radical atoms **catalyse** the decomposition of ozone, due to these reactions, because they are regenerated. (They provide an alternative route with a lower activation energy)

These reactions contributed to the formation of a hole in the ozone layer.

$$Cl^{\bullet} + O_3 \rightarrow ClO^{\bullet} + O_2$$

$$ClO^{\bullet} + O_3 \rightarrow 2O_2 + Cl^{\bullet}$$

Overall equation

$$2\,O_3 \rightarrow 3\,O_2$$

The regenerated Cl radical means that one Cl radical could destroy many thousands of ozone molecules.

Legislation to ban the use of CFCs was supported by chemists and that they have now developed alternative chlorine-free compounds.

HFCs (Hydro fluoro carbons) e.g. $CH_2FCF_3$ are now used for refrigerators and air-conditioners. These are safer as they do not contain the C-Cl bond.

The C-F bond is stronger than the C-Cl bond and is not affected by UV.